



Synthesis of Bridged Oligophenylene Laser Dyes

Final Technical Report

by

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13. ABSTRACT (Maximum 200 words) Bridged hydrocarbon oligophenylene laser dyes with 6 and 8 benzene rings with differing numbers (1-4) of dipropylmethylene bridges have been synthesized. These molecules are highly fluorescent in the 400-430 nm region. The structure of the previously synthesized unbridged methoxy-substituted azaterphenyl, 4-PyMPP, has been shortened by the insertion of a 2,6-disubstituted naphthalene for a 4,4'-biphenylene subunit. Both the naphthalene analog and 4-PyMPP itself have been lengthened by a phenylene unit; one bridging group was also present in the latter, an azaquaterphenyl. After quaternization of the nitrogen all three azaoligophenylenes were fluorescent. The naphthalene analog fluoresced at the shortest wavelength (480 nm in the blue green) while the longer molecules both fluoresced in the yellow (550+ nm). Six new compounds have been submitted to MICOM for testing as flashlamp pumped laser dyes. The naphthalene azaoligophenylene lased, but with a high threshold and a low (2 mjoule) output. The hydrocarbon oligophenylenes are still being evaluated to ascertain the optimal bridging pattern for flashlamp-pumped lasing.			
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PART I: STATEMENT OF THE PROBLEM STUDIED

The United States Army has been interested in exploring various applications of dye laser technology. The Army Missile Command (MICOM) has been testing new chemical substances for their potential as laser dyes which could operate in flashlamp pumped dye lasers. We chose to concentrate our efforts equally in two areas of the synthesis of new dyes which can be broadly classed as oligophenylenes. The first area involved new hydrocarbon oligophenylenes for the 400-430 nm region of the visible spectrum. The second area involved oligophenylenes substituted with electron-donating and electron-withdrawing substituents at opposite ends of the long axis of the chromophore (linearly polarized oligophenylenes). This type of molecule has been observed to have a very large Stokes shift in alcohol solvents and thus can provide potential laser dyes in the blue-green to the yellow (480-570 nm) regions of the visible spectrum. An additional desirable property of this latter type of compound is its solubility in non-flammable water--alcohol mixtures.

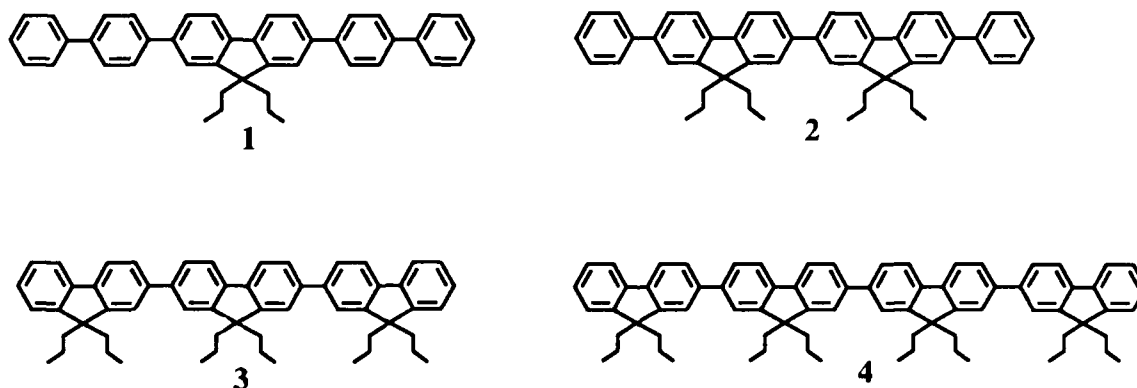
The parent oligophenylene with six benzene rings, sexiphenyl (mp 465°), is virtually insoluble in organic solvents at all but highly elevated temperatures (Kovacic, 64). Thus it cannot be tested as a laser dye. In our work with quaterphenyls bridged with dipropylmethylene groups (Kauffman/Kelley, 87), we found that the bridging confers marked increases in solubility to the dyes without adversely affecting their useful lifetime as laser dyes. The longer the extended system of benzene rings in an oligophenylene, the longer the wavelength of its fluorescence emission, the higher its extinction coefficient, and the greater its anticipated lifetime in an operating dye laser.

During the period of this contract we have sought to obtain fundamental knowledge about the relationship of bridged oligophenylene structure to its photophysical properties by synthesizing a series of these compounds for spectroscopic and laser testing. We prepared a series of three sexiphenyl dyes with different bridging patterns to determine what degree of bridging is necessary to achieve the solubility needed for the dye. We also hoped to ascertain what effect differing the numbers of bridges has on the ultraviolet absorption maximum and extinction coefficient of the series of oligophenylenes. Ultimately we hoped to answer the question posed by Jim Bentley (Bentley 87) 'How much restricted rotation (by bridging) in an oligophenylene chromophore will allow the optimum lasing?'

In the area of linearly polarized oligophenylenes, we sought to answer two questions. First what would be the effect of replacing a 4,4'-biphenyl spacing group by the 2,6-disubstituted naphthalene chromophore and secondly, what structural features would make it possible to allow conjugation between the electron donor and acceptor groups in molecules longer than three benzene rings. Specifically we sought to introduce one bridging group into a four-ring aromatic system to see if conjugation and thus enhanced Stokes shift could be maintained in larger systems.

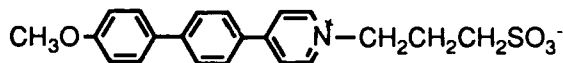
PART II: SUMMARY OF THE MOST IMPORTANT RESULTS

A total of eight new compounds for use as laser dyes have been synthesized. Four compounds belong to the hydrocarbon oligophenylene class. Three of these are symmetrical sexiphenyls with one, two and three dipropyl-methylene bridges between the rings (**1-3**). The fourth oligophenylene is the first very pure octaphenyl, **4**. This octaphenyl contains four dipropyl-methylene bridges. Only the fluorescence spectrum and fluorescent emission maximum (408 nm) of **2** are known from earlier work (Wunderly/Kauffman 90). We anticipate that the compounds **1-4** will constitute a series of laser dyes emitting in the 400-430 nm range.

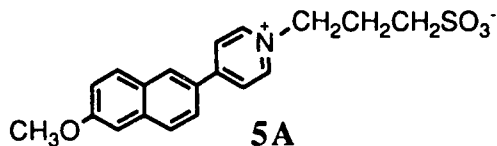
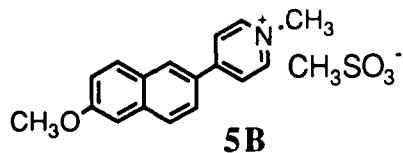
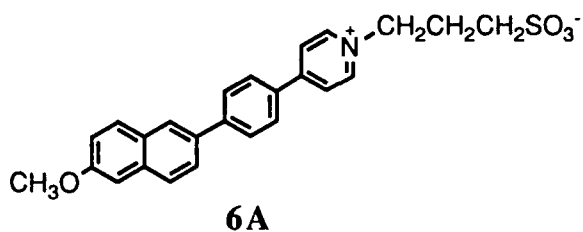
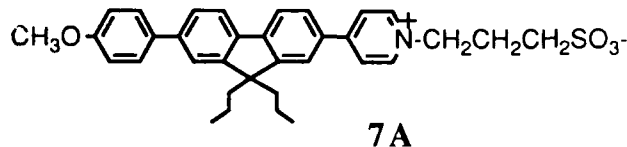


In the area of linearly polarized oligophenylenes, we have synthesized two new dyes in which the 2,6-disubstituted naphthalene nucleus has replaced a 4,4'-biphenyl group in the known laser dye, 4-PyMPP (laser data: Bentley 87). These new compounds **5A** and **5B** were submitted to MiCOM for testing and found to have a maximum fluorescence emission at 481 nm--a substantial blue shift from their 4-PyMPP which

lased at 546 nm in methanol. In lasing tests **5B** did lase, but it suffered from a high threshold and a reduced light output (ca. 2 mJoules)



4-PyMPP

**5A****5B****6A****7A**

(Davenport 90).

Subsequently we prepared a higher homolog of **5A** which contains an extra phenylene group between the naphthalene and the pyridine rings. This compound **6A** has not been submitted for testing, because of the weak fluorescence emitted by alcohol solutions in which **6A** was only very slightly soluble. We have also prepared a higher homolog of the 4-PyMPP which contains one bridge in its structure. Compound **7A** which fluoresces in the yellow in alcohol solution appears to demonstrate that the conjugative effect of the methoxy group with the pyridinium cation can be transmitted through four rings if two of the rings are bridged.

PART III: DISCUSSION OF SYNTHETIC METHODS

(a) Purification of 2-bromo-9,9-dipropylfluorene (**14**).

The long-standing problem of the contamination of the key intermediate, 2-bromo-9,9-dipropylfluorene (**14**) by its 2,7-dibromo analog (**15**) has been solved by the purification of a new liquid intermediate in a spinning band distillation apparatus. The new three-step synthesis of **14** is depicted in Scheme I. In our previous work, in

which fluorene was monobrominated, the 2-bromofluorene intermediate was a solid melting about 110-12°. Although we tried on several occasions to distil the solid through a heated apparatus, we were unable to fractionate the solid from its accompanying 2,7-dibromo derivative. On a separate occasion we attempted to distil the 92:8 mixture of **14** and **15** (mp 70-71°) resulting from previously described syntheses (Ghiorghis 88) by means of the spinning band apparatus. Apparently because of the high boiling point of the product, our teflon spinning band froze during the distillation, and we were unable to collect any purified distillate.

Subsequently it came to our attention that a unique, quantitative synthesis of 9-monoalkyl fluorenes was described in the literature (Schoen 63). Employing this method we obtained 9-propylfluorene in an improved yield, and found that there is no trace of dialkylation occurring in the process. The liquid 9-propylfluorene (**12**) could then be brominated by one equivalent of N-bromosuccinimide (NBS) to a mixture of unreacted **12** (20%), 2-bromo-9-propylfluorene (**13**) (60%), and 2,7-dibromo-9-propylfluorene (20%). Distillation of this mixture allowed the recovery of **12** (bp 90° @0.01 torr) and the desired 2-bromo-9-propylfluorene **13** (bp 110 @ 0.01 torr). Gas chromatographic assay indicated that less than 0.2% (no peak observed) of the dibromo analog was present in the material.

The liquid bromide **13** was then alkylated with propyl bromide and potassium t-butoxide to give the 2-bromo-9,9-dipropylfluorene (**14**). On crystallization this material melted at 74.5-75° and gave only one peak in the gas chromatograph. An interesting observation is the strikingly different color progression observed in the synthesis of 9,9-dialkylfluorenes when starting with a pure *monoalkyl* fluorene or with an *unalkylated* fluorene. With the monoalkyl fluorene the red and purple colored carbanion intermediates fade totally to a gray color when the reaction is completed. In the dialkylation of fluorene or 2,7-dibromofluorene, the initially red solution progresses to a deep purple as the reaction proceeds. The final purple color never faded by itself, and the color was very slow to decolorize even in the presence of somewhat acidic proton donors (sometimes warming with acids was required to discharge the purple color. There must be some highly colored compound other than dialkylfluorenes produced when fluorene itself is dialkylated in one pot. No such colored material is produced when the second alkyl group is introduced into the previously alkylated 9-alkylfluorene.

(b) Preparation of Sexiphenyl Laser Dyes 1 - 3.

A recent literature method (Negishi 86) involves the use of two equivalents of t-butyllithium to prepare aryllithium intermediates which are subsequently converted to their organozinc analogs before they are coupled via the palladium (II) (dppb) catalyst to the appropriate aryl bromides. The use of two equivalents of t-butyl lithium is necessary since the second mole dehydrohalogenates the t-butyl bromide produced in the initial lithium-halogen exchange. If this alkyl halide were not removed, it would compete with the aryl halide in the subsequent coupling reaction. The extremely high basicity of t-butyllithium requires that it not be brought in contact with the solvent THF even at dry-ice temperatures. Thus the initial low-temp. lithium-bromine exchange must be carried out in the less reactive diethyl ether solvent.

When bromobiphenyl **16** was the starting material (Scheme II), the initial reaction with t-butyllithium gave a stirrable solution in which temperature control and mixing were not such a problem. A minor fluorescent byproduct having a lower R_f value on thin layer chromatography was produced along with **1**. Repeated recrystallization of **1** was effective, however, in removing all but a trace of the impurity.

When **14** is the starting material in the reaction with t-butyl lithium (Scheme III), its lithium derivative has such low solubility in ether that an almost unstirrable paste is produced by the initial exchange. This makes difficult both mixing and temperature control as the second equivalent of t-butyllithium is added. As noted above there are no impurities in **14** which could be blamed for any byproduct formation. Thus it is not clear why the samples of **3** and **4** prepared from this starting material contained a trailing fluorescent impurity, apparently a higher oligophenylene. The presence of the impurity was extremely problematic with sexiphenyl **3**, because repeated recrystallizations of the compound did not seem to improve the melting point which remained depressed by more than 10°. In order to free **3** from higher oligophenylenes, the sample was preadsorbed on silica gel and was continuously extracted with hexane in an Ace-Kauffman column. This allowed the recovery of more than a gram of **3** with a melting point equal to the milligram quantities obtained earlier by preparative tlc (Ghiorghis 88).

In dramatic contrast to the difficulties encountered in purifying sexiphenyl **3**, octaphenyl **4** was obtained with an analytical-sample melting point in 77% yield directly from the initial Ace-Kauffman purification procedure. The contrast is explained, in part, in that the octaphenyl **4** is much less soluble in cyclohexane than **3**, and thus all impurities, including those of the presumably higher oligophenylenes, remain in the cyclohexane mother liquors. The striking difference in solubility is reminiscent of the solubility (and melting point) alternation observed in the family of simple dicarboxylic acids. Thus dicarboxylic acids with even numbers of carbons melt higher and are less soluble than their next higher homolog which has an odd number of carbons. Perhaps we are here encountering a similar phenomenon where oligophenylenes with even numbers of fluorene units are less soluble than those with odd numbers of fluorenes. Further syntheses would be required to verify this analogy, however. Another striking difference between **3** and **4** is that the former is perfectly white when pure while the latter is a light yellow in color indicating that it is absorbing light at a longer wavelength.

(c) Preparation of Naphthylpyridine Laser Dyes 5A , 5B and 6A.

The commercial availability of 6-bromo-2-naphthol (**19**) provided an easy route to push-pull laser dyes containing a naphthalene ring as shown in Scheme IV. The methyl ether (**20**) was easily converted into the piperidinol derivative **21** which in a single high-temperature step could be dehydrated and aromatized by the general procedure we reported earlier (Kauffman/Kelley 87b). The resulting pyridine **5** was quite soluble in most solvents, and only 1,2-dimethoxyethane would give back crystals. Pyridine **5** could probably be obtained in higher yield if a better recrystallization solvent were found. However, pure **5** could be quaternized slowly (48 hrs reflux required) in acetonitrile or quickly (<15 mins.) in benzonitrile at elevated temperatures. The quaternary derivative from methyl methanesulfonate (**5B**) was, like the parent compound, quite soluble in many solvents and a good bit was lost in recrystallization. The much lower solubility of the zwitterionic derivative, dye **5A**, allowed its isolation in high yield even after recrystallization.

The preparation of the higher homolog of **5**, the naphthylphenylpyridine **6** shown in Scheme V, required the preparation of a starting material not available from commercial sources. Indeed the only literature reports of **22** are by methods which give inherently low yields due to isomer formation (Butterworth 40, Walter 83) or are not easily reproducible (Katritzky 80). Thus we felt it necessary to devise a new method for the preparation of **22** free of any positional isomer. We were able to prepare quite pure **22** by the Grignard coupling reaction of an excess p-chlorophenylmagnesium bromide with 4-chloropyridine hydrochloride. Pyridine **22** could be dissolved in acid to remove the impurity of 4,4'-dichlorobiphenyl produced during the Grignard formation. Pure **22** as the free base could then be coupled with the Grignard reagent from bromonaphthalene **20** using nickel acetoacetate as the catalyst (Clough 76, Hayashi 81) to produce the desired azaarene **6**.

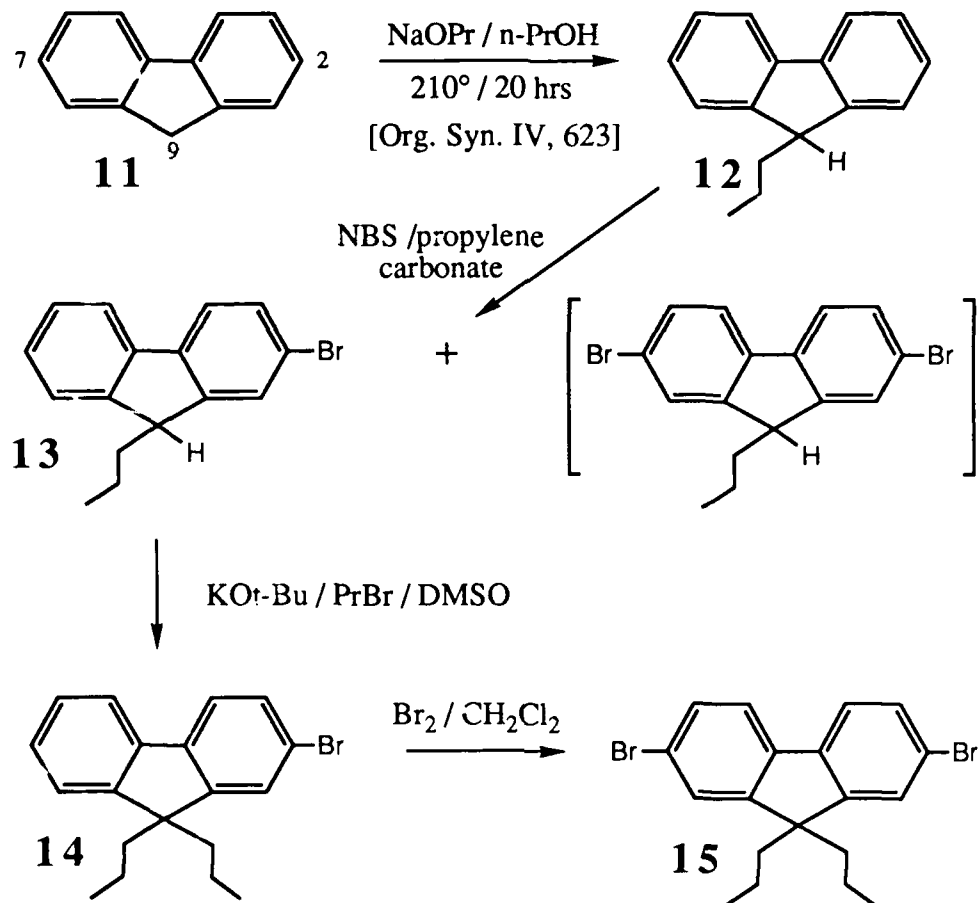
(d) Preparation of the Bridged Terphenylpyridine Laser Dyes 7A.

Our original proposal (prepared in the summer of 1987) contained several examples of four-ring (quaterphenyl) structures which contained a methoxy group attached to one end of the chromophore while a 4-substituted pyridine ring constituted the other end. Of paramount importance was to synthesize a molecule in which there was at least one bridge between two adjacent rings. The bridging would leave just two freely-rotating aryl-aryl bonds in the molecule and thus greatly improve the possibility that the conjugated system would in fact become fully planarized in the excited state.

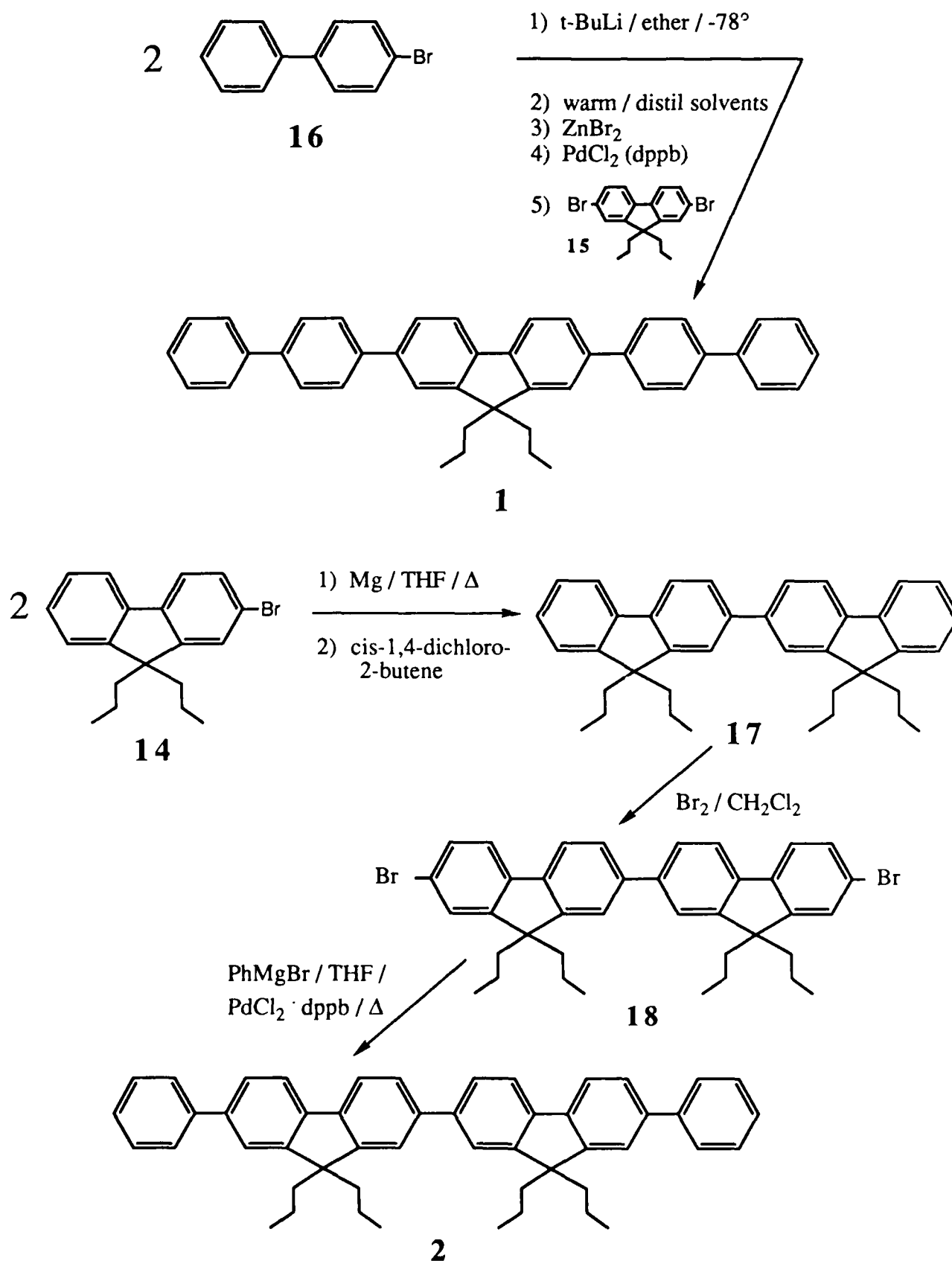
We have successfully achieved the synthesis of one example of this type of molecule, pyridine **7**. As shown in Scheme VI, this synthesis was achieved by elaboration of fluorene **14** into the methoxyterphenyl **23** by the palladium-catalyzed Grignard coupling. Bromination of **23** was not clean as both the activated 7-position on the fluorene and the positions ortho to the methoxy group react readily with N-bromosuccinimide. We had earlier observed this competitive bromination in the halogenations of 4-methoxybiphenyl and 2-methoxy-9,9-dipropylfluorene (Kauffman/Kelley 86 and Kelley/Kauffman 87). Purification of the desired bromofluorene derivative **24** was easily achieved by crystallization as the other brominated materials proved more soluble in hexane.

Bromofluorene **24** was then converted to the 4-arylpiperidinol **25**, and the later was aromatized over palladium on carbon at elevated temperature to produce the pyridine **7**. The quaternization of **7** by propane sultone in hot benzonitrile gave the sulfopropyl zwitterion **7A** which fluoresces yellow in alcohols and seems quite soluble in a range of solvents. Although excellent elemental analyses were achieved for all the compounds shown in Scheme VI, the homogeneity of the fluorescent species in **7A** has not been satisfactorily verified. It is premature to give this compound what might be its only test as a laser dye without further verification of its purity.

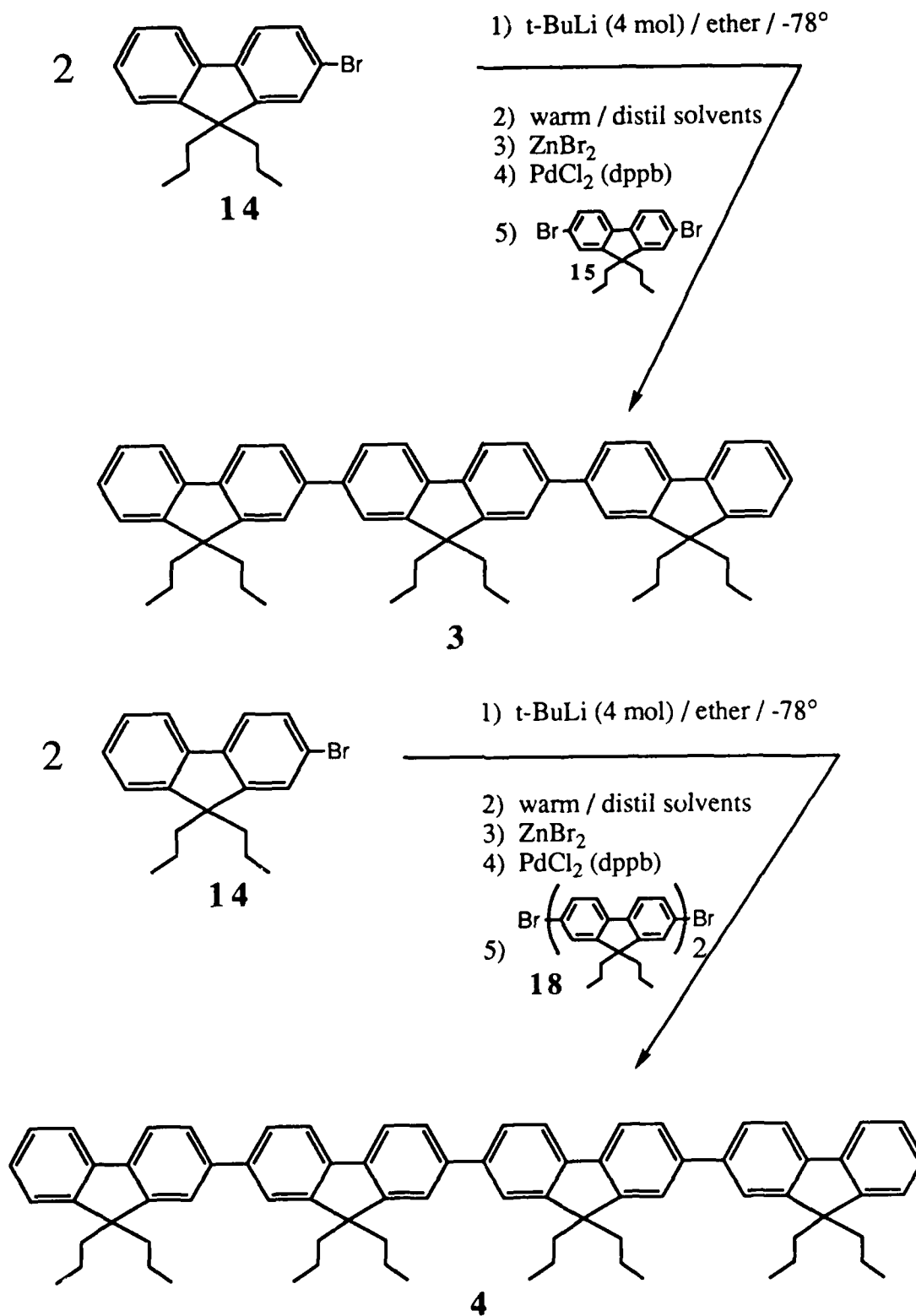
Scheme I: Preparation of Brominated Intermediates, Pure 2-Bromo-9,9-dipropylfluorene (14) and 2,7-Dibromo-9,9-dipropylfluorene (15)



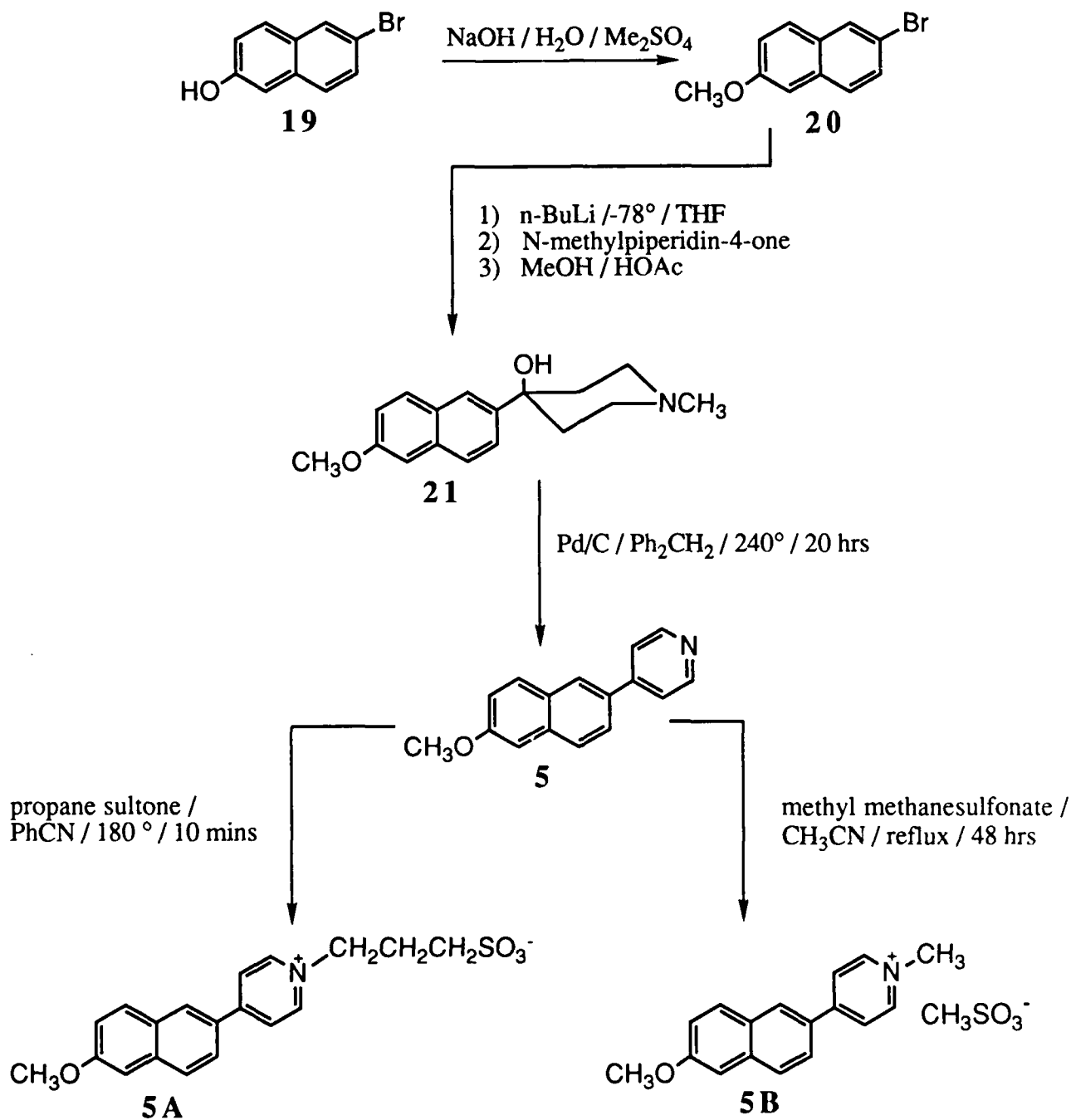
Scheme II: Preparation of Bridged Sexiphenyls **1** and **2**.



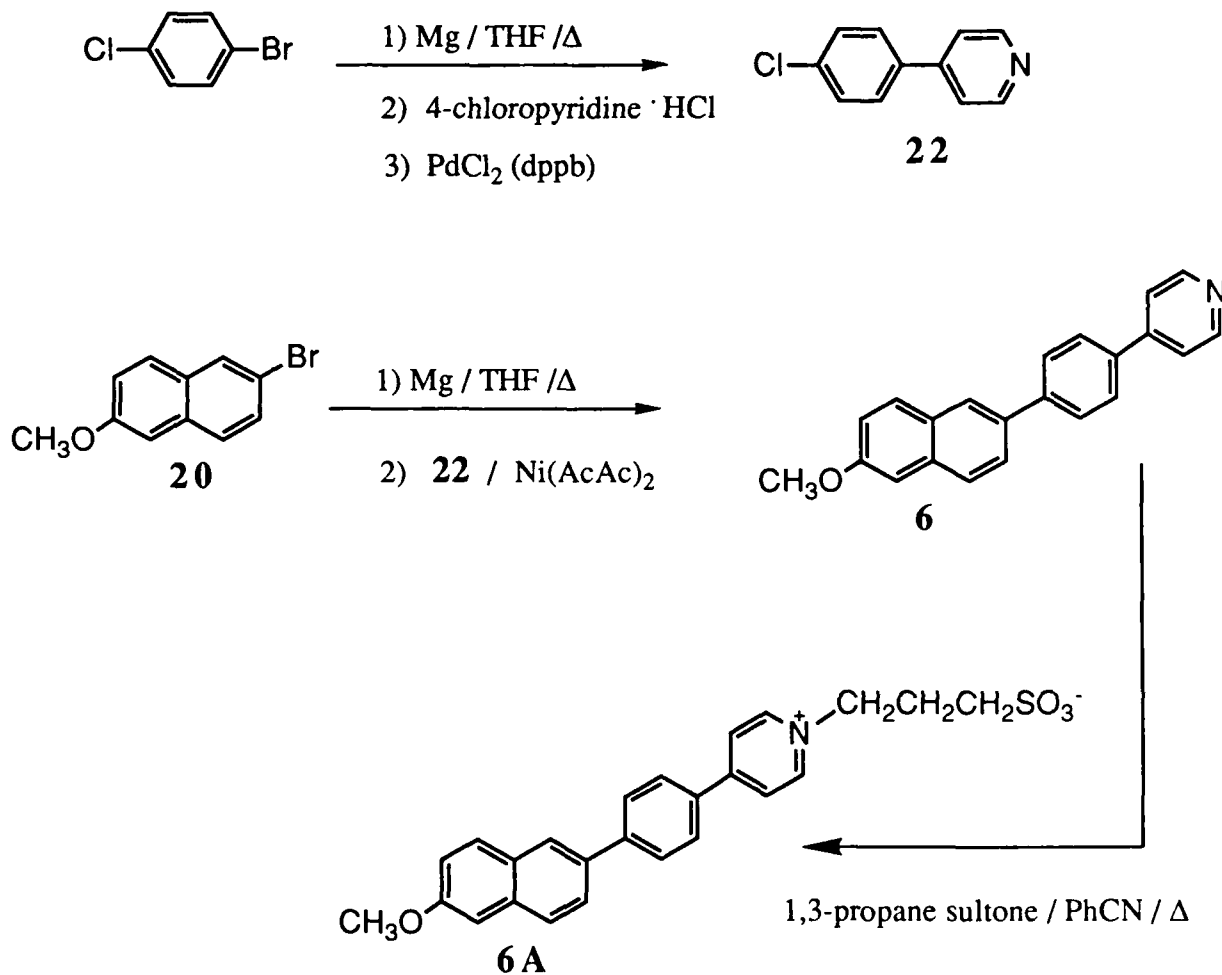
Scheme III: Preparation of Sexiphenyl 3 and Octaphenyl 4



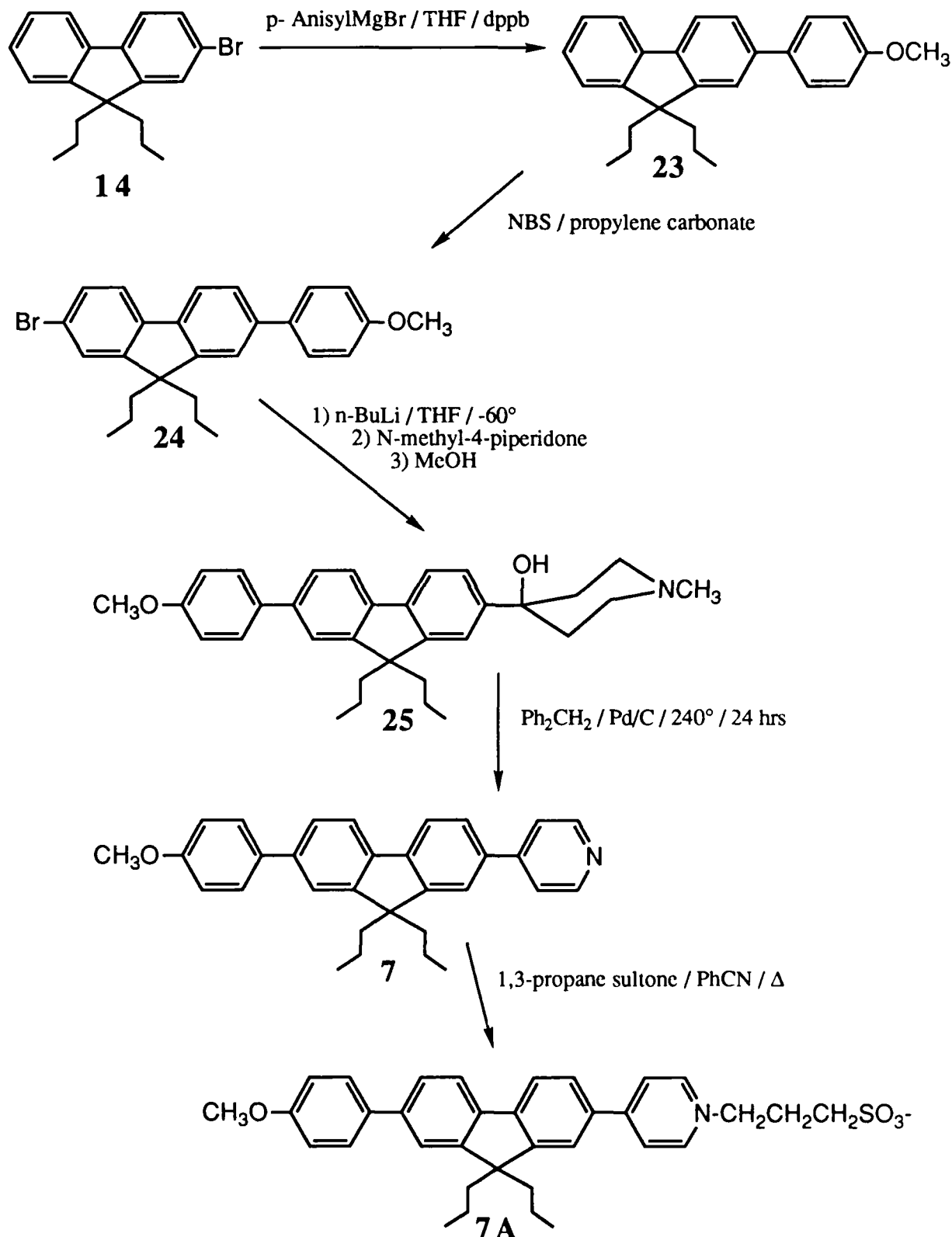
Scheme IV: Preparation of 4-(6-Methoxynaphth-2-yl)pyridine



Scheme V: Preparation of 4-[4-(6-Methoxynaphth-2-yl)phenyl]pyridine (6).



Scheme VI: Preparation of 4-(7-[4-Methoxyphenyl]-9,9-dipropylfluoren-2-yl)pyridine (7).



Part IV: EXPERIMENTAL

9-Propylfluorene (12)----(Procedure of Schoen 63). Into a 1L stainless steel Paar bomb was loaded fluorene (**11**, 113 g, 0.68 mol) and a solution of sodium propoxide in 1-propanol (prepared by dissolving 23 g (1.0 mol) of sodium in 450 mL of 1-propanol). The bomb was sealed and stirred internally with a teflon-coated stirring bar while it was heated on a sand bath (bath temp 220°) for 60 hrs. After it was cooled the solution was transferred to a 2L beaker with the aid of a small volumes of heptane and water. The excess base was neutralized with concentrated hydrochloric acid (15 mL) and the mixture was extracted with heptane (3x150 mL). The combined heptane extracts were washed with water (3x200 mL) and dried over anhyd. sodium sulfate. The heptane was removed under reduced pressure to give 160.3 g of crude product. This was distilled under reduced pressure to give three fractions the 1st weighed 45.7 g, (bp to 175° @15 mm), the 2nd fraction weighed 63.5 g, (bp 115-126° @ 0.35 mm) and the 3rd fraction weighed 44 g with the same boiling range. The latter two fractions were judged to be pure **12** by nmr spectroscopy. The addition of a small amount of fluorene to the nmr tube indicated that there was no trace of unreacted fluorene present in the distilled product.

¹H-nmr (neat) δ 0.65 (t, 3H, -CH₂CH₂CH₃), 1.02 (m, 2H, -CH₂CH₂CH₃), 1.65 (m, 2H, -CH₂CH₂CH₃), 3.62 (t, 1H, H-9), 7.1 (m, 6H, H's 1-3, 6-8), 7.4 (m, 2H, H's 4,5).

2-Bromo-9-propylfluorene (13)-----A mixture of **12** (106.4 g, 0.51 mol), NBS (90.8 g, 0.51 mol) and propylene carbonate (300 mL) was stirred at 60° for half an hour. Water (300 mL) and hexanes (500 mL) were added and the hexane layer was separated, was washed with 5% NaOH and water (3x 300 mL) and was dried with anhydrous sodium sulfate. After filtration the solution was evaporated to remove solvent. Distillation of the residue under reduced pressure gave 121.5 g of yellow liquid. Spinning band fractional distillation of the yellow liquid gave 83.9 g (57.3%) of **13** as a slightly yellowish liquid (bp 110° @0.005 mm).

^1H -nmr (CDCl_3) δ 0.80 (t, 3H, $-\text{CH}_2\text{CH}_2\text{CH}_3$), 1.10 (m, 2H, $-\text{CH}_2\text{CH}_2\text{CH}_3$), 1.70 (m, 2H, $-\text{CH}_2\text{CH}_2\text{CH}_3$), 3.62 (t, 1H, H-9), 7.08 (m, 5H, H's 1,3, 6-8), 7.28 (m, 2H, H's 4,5).

Anal. Calcd for $\text{C}_{16}\text{H}_{15}\text{Br}$: C, 66.91; H, 5.26; Br, 27.82.

Found: C, 69.26, H, 5.18.

2-Bromo-9,9-dipropylfluorene (14)-----A mixture of **13** (77.5 g, 0.27 mol) and potassium t-butoxide (45.5 g, 0.405 mol) was partially dissolved in DMSO (200 mL) with stirring under nitrogen, and 1-bromopropane (49.6 g, 0.405 mol) was added dropwise while the mixture was maintained at 40-50°. The mixture was then stirred at room temp. for an additional 1.5 hrs. During this time the deep red color initially present in the solution faded to a pale gray. Methyl t-butyl ether (300 mL) and water (200 mL) were added and the upper layer was separated. The lower layer was extracted further with methyl t-butyl ether (2x 100 mL). The combined organic layer was washed with water (3x 100 mL), and was dried with anhyd. sodium sulfate. After filtration the solution was evaporated to remove the solvent. The residual oil was crystallized from 95% ethanol (380 mL) containing acetonitrile (80 mL) to give 70.7 g (79.5%) of nearly colorless crystals of **14**, mp, 74.5-75° as the first crop. The second crop weighed 9.7 g, mp 73-5°, bringing the total yield to 90%.

Anal. Calcd for $\text{C}_{19}\text{H}_{21}\text{Br}$: C, 69.30; H, 6.43; Br, 24.27.

Found: C, 69.22, H, 6.44.

2,7-Dibromo-9,9-dipropylfluorene (15)-----To a solution of crude **14** (2.2 g, 0.61 mol) in dry methylene chloride (175 mL) was added a solution of bromine 32 mL, 0.65 mol) in methylene chloride (125 mL) all at once. The mixture was refluxed with stirring for 2 hrs. The hydrogen bromide gas which evolved was led to a solution of aqueous sodium and ammonium hydroxides. To the reaction mixture were added a solution of 200 mL of sodium bisulfite (25 g) and an additional 400 mL of methylene chloride. The organic layer was separated, was washed with 300 mL of a saturated solution of sodium bicarbonate and was washed with water (2x 300 mL). The solution was dried over sodium sulphate and was filtered and reduced to half its volume under reduced pressure. On standing crystalline **15** precipitated 148.2 g (60%), mp 135-136.5° [Lit. mp 136-7°, Ghiorghis 88]. Concentration of the mother liquor (2x) gave a second (22.7 g) and a third (28.9 g) crop of **15**. The total yield of **15** was 80.6 %.

2,7-Bis(biphenyl-4-yl)-9,9-dipropylfluorene (1)----- To a dry-ice cooled paste of 4-bromobiphenyl (Kodak) **16** (32.2 g 140 mmol), formed by cooling a solution of **16** in 130 mL of anhyd. ether, was added dropwise t-butyllithium (1.7 M in pentane, 165.2 mL, 280 mmol) with stirring under nitrogen. After the reaction mixture was stirred at -65-75° for one hour, it was warmed to r.t., was stirred for another hour and was distilled under water-aspirator pressure into a dry-ice-cooled trap. To the residue was added THF (200 mL). The resulting solution was added under nitrogen via cannula to zinc bromide (31.5 g, 140 mmol, Aldrich 21,632-1, dried at 180°/0.05 torr for 3 hrs). The resulting slightly cloudy straw-yellow solution was stirred for 13 hrs. To the mixture were added PdCl₂ (dppb) (370 mg) and dibromide **15** (16.1 g, 40 mmol). The mixture was stirred under nitrogen at r.t. for two days. A small amount of methanol was added and the mixture was evaporated to remove the solvents. Methanol (300 mL) was added to digest the residue and the solid was collected by filtration. The solid was purified by passing it twice through an Ace-Kauffman columns packed with 30 g of silica gel, 20 g of alumina (first time) and 20 g of silica gel and 20 g of alumina (second time) to give 17.2 g (77.6%) of white solid **1**, mp 244-250°. This solid was recrystallized three times from o-xylene (85, 80, and 60 mL) to give 12.1 g (55%) of **1** as a white solid, mp 252-55°.

Anal. Calcd for C₄₃H₃₈: C, 93.10; H, 6.90.

Found: C, 93.21, H, 6.92.

9,9,9',9'-Tetrapropyl-2,2'-bifluorene (17)-----

Freshly ground magnesium turnings (1.48 g 60.7 mmol) in a 100 mL flask were heated to 200° for 10 mins under a stream of nitrogen gas. After cooling, 20 mL of THF and 20.0 g (60.7 mmol) of **14** were added to the flask. The mixture was heated to reflux and maintained there for 5 hrs during which time much of the magnesium dissolved. The flask was cooled to room temp. and cis-1,4-dichloro-2-butene (2.15 g, 24.3 mmol, Aldrich 19,570-7) was added dropwise to the solution. A gas was immediately evolved, and a solid precipitated throughout the addition. After one hour, methanol (50 mL) was added to the mixture. Some exotherm was noted. The solid collected by filtration weighed 8.37 g on drying. Recrystallization of this material from 60 ml of ethyl acetate gave 5.68 g (37.5%) of **17**, mp 180-2° [lit. mp 182-3°, Ghiorghis 88], which showed only a very faint trailing fluorescent impurity on tlc (silica gel/cyclohexane; R_f = 0.4)

7,7'-Dibromo-9,9,9',9'-tetrapropyl-2,2'-bifluorene (18)

----To a mixture of 10.0 g (0.02 mol) of **17** in 40 mL of methylene chloride was added 2.05 mL of bromine in several portions. The bromine color faded after each addition, the initial solid dissolved, and later another solid precipitated. The addition was completed in one hour. The mixture was cooled in an ice bath. The solid was filtered and washed with a little CH₂Cl₂ and with 50 mL of 10% NaHSO₃. The dry white solid weighed 9.77 g. On recrystallization from 50 mL of chloroform containing 1.5 mL of ethanol 6.8 g (52%) of **18**, mp 265-7°, [lit. mp 269-71° (Ghiorghis 88)] was obtained. The material was submitted for elemental analysis because the earlier data [Ghiorghis 88] was not in acceptable agreement with theory.

Anal. Calcd for C₃₈H₄₀Br₂: C, 69.52; H, 6.14.

Found: C, 69.44, H, 6.01.

7,7'-Diphenyl-9,9,9',9'-tetrapropyl-2,2'-bifluorene (2)--

A flask was charged with 0.62 g (0.025 mol) of ground magnesium (heated and cooled under nitrogen), 35 mL of THF and 4.0 g of bromobenzene. The mixture was refluxed overnight and almost all of the magnesium was consumed. This solution of phenylmagnesium bromide was then transferred via cannula to a solution of 2.89 g (4.26 mmol) of dibromide **18** and 350 mg of PdCl₂ (dppb) dissolved in 35 mL of THF. The resulting mixture was stirred and refluxed under nitrogen for 40 hrs. Methanol (10 mL) was added and an exotherm noted. The removal of the solvents under reduced pressure gave a dark residue, which on trituration with 60 ml of methanol gave a solid weighing 3.7 g on filtration and drying. This solid was extracted through 60 g of silica gel and 20 g of alumina in an Ace-Kau column with refluxing cyclohexane for 144 hrs. Concentration to dryness gave 2.8 g of **2**, mp 230-2. This sample was recrystallized from 150 mL of boiling n-heptane with a hot filtration to give 2.00 g of **2**, mp 238-40°. {YXQ-1-79}

Anal. Calcd for C₅₀H₅₀: C, 92.26; H, 7.74.

Found: C, 92.49, H, 7.92.

2,7-Bis(9,9-dipropylfluoren-2-yl)-9,9-dipropylfluorene (3)-----

On cooling to -80° a solution of **14** (19.8 g, 60 mmol) in 60 mL of diethyl ether formed an unstirrable paste. To this paste was added dropwise 71 ml of t-butyllithium (1.7 M, Aldrich) in pentane. During the addition, the temperature of the mixture was kept below -50°. After the reaction was held at -75° for an hour it was warmed to

room temp., but it did not become stirable until the temperature was above 0°. After the reaction was stirred at room temp. for another hour, the solvent was distilled into a dry ice-cooled trap under water aspirator pressure. The residue from the distillation was dissolved in 200 mL of THF, and this solution was in turn transferred to a flask containing a solution of 13.5 g (60 mmol) of zinc bromide (dried in the flask at 180°/0.01 torr) in 10 mL of THF. The resulting solution was straw-yellow in color. This solution was stirred at room temp. for 12 hrs. To the solution was added the dibromide **15** (8.2 g, 20 mmol) and 250 mg of PdCl₂ (dppb), and the mixture was stirred under nitrogen for 3 days. A small amount of methanol was added to the mixture, and all of the solvent was removed under reduced pressure. The residue was diluted with 300 mL of methanol and the mixture was stirred at for 20 min. and was filtered. The solid was washed with methanol air-dried and placed atop 30 g of silica gel (grade 923, 100-200 mesh) and 30 g of neutral alumina in an Ace-Kauffman column. The solid was extraced with cyclohexane for 60 hrs to give 12.87 g (86%) of a solid, mp 189-92°. The tlc of this material (cyclohexane/silica gel) indicated that only a trace of bifluorene (**17**) was present, but a large quantity (as much as 10 %) of a slower moving fluorescent impurity was present along with the desired product **1**. The product was recrystallized from 2-methoxyethanol (500 mL) to give 12.81 g, mp 192-196°. A second crystallization from heptane (200 mL) gave 10.85 g still melting 192-196° (melt clears at 200°). Tlc (cyclohexane/silica) still shows two fluorescent spots (the second at the R_f of **4**). {YXQ-1-15/6}

2,7-Bis(9,9-dipropylfluoren-2-yl)-9,9-dipropylfluorene (3**)**----- A solution of 2-bromo-9,9-dipropylfluorene (**14**, 23 g, 70 mmol) in 80 mL of anhydrous ether was cooled to -70°. t-Butyllithium (1.7 M in pentane, 83 mL, 140 mmol) was slowly added to the mechanically stirred solution while the temperature was maintained below -60°. After the addition the mixture was stirred at -70° for one hr, and then was allowed to warm slowly to room temperature. The mechanical stirrer was repaced by a magnetic stirrer, and the mixture was evaporated under aspirator pressure at room temp. to remove all volatile solvents. Anhydrous THF (200 mL) was added to dissolve the residue. The solution was in turn transferred to a solution of zinc bromide (15.8 g, 60 mmol, Aldrich 21,632-1, predried 180°/0.01 torr/3 hrs) in 50 mL of THF. After the mixture was stirred for half an hour at room tmeperature, a mixture of 2,7-dibromo-9,9-

dipropylfluorene (**15**, 8.2 g, 20 mmol) and PdCl₂ (dppb) (280 mg) was added. The mixture was stirred at room temperature for 24 hr and then refluxed for 14 hrs. Methanol (10 mL) was added slowly with stirring and the solution was concentrated to dryness under reduced pressure. The residue was triturated with 250 mL of methanol and filtered to give 17.5 g of solid. Recrystallization of the solid from 2-methoxyethanol gave 10.5 g of solid, mp 196°. This solid was placed atop of silica gel (60 g) and alumina (30 g) in an Ace-Kau column and extracted with n-hexane for 48 hrs. On cooling 6.8 g of **3**, mp (softens 195°) 198-202°. By concentration of the solvent and cooling a second (1.43 g) and a third (2.22 g) crop of **3** was obtained. Various portions of this crude **3** were *preadsorbed* on silica gel and extracted in the Ace-Kau apparatus with hexanes to give increasingly pure samples of the sexiphenyl, **3**. The best sample 1.7 g was white, and after recrystallization from n-heptane (80 mL) gave 1.2 g (softens 202°, mp 207-8°). One other sample (0.35 g) melted cleanly 207-9°. Tlc analysis of these samples of **3** showed no trace of a fluorescent impurity with an R_f value corresponding to **4**. {YXQ-1-72/5}

Anal. Calcd for C₅₇H₆₂: C, 91.63; H, 8.37.

Found: C, 91.40, H, 8.31.

2,7'-Bis(9,9-dipropylfluoren-2-yl)-9,9,9',9'-tetrapropyl-2,2'-bifluorene (4)-----A solution of 13.2 g (40 mmol) of **14** in 60 mL of anhydrous ether was cooled to -70° with mechanical stirring. *t*-Butyllithium (47 mL, 80 mmol, Aldrich 1.7M in pentane) was added while the temperature was kept below -60°. The mixture was stirred at that temperature for one hour, and the mechanical stirrer was exchanged for a magnetic bar. The mixture was evaporated almost to dryness into a dry ice-cooled trap under water aspirator vacuum. The residue was dissolved in 200 mL of THF, and the solution was transferred under nitrogen via cannula to another flask containing 15.8 g of zinc bromide (9 g, 40 mmol, dried 180°/0.01 torr.). The yellow solution was stirred at room temperature for half an hour and a mixture of solids, **18** (6.57 g, 10.0 mmol) and PdCl₂ (dppb) (300 mg), were added. The resulting solution was refluxed for 20 hrs, cooled to room temperature and a small volume of methanol was added. The solvents were removed under reduced pressure and the residue was triturated with 20 mL of methanol. The solid collected by filtration (10.99 g) was placed atop silica gel 50 g and alumina 20 g in an Ace-Kau column and eluted with boiling cyclohexane for a week. The

cyclohexane solution was filtered to give 7.65 g (77% yield) of light yellow **4** (containing only a slight trace of **3** by tlc analysis), mp 267-9°. Recrystallization of 0.5 g of **4** from 5 mL of toluene gave the analytical sample with no change in melting point. {YXQ-1-80}

Anal. Calcd for C₇₆H₈₂: C, 91.70; H, 8.30.

Found: C, 91.53, H, 8.40.

2-Bromo-6-methoxynaphthalene (20)----- A solution of 6-bromo-2-naphthol (**19**, 53 g, 0.237 mol; Aldrich B7,340-6) in 130 mL of sodium hydroxide (10 g) solution was cooled in an ice-water bath as dimethyl sulfate (22.4 mL, 29.8 g, 0.237 mol, Aldrich D18,630-9) was added dropwise with stirring under nitrogen. The mixture was warmed to 70-80° and stirred for one hour. The solution was cooled and the solid was filtered and washed in the filter with 10% aq. sodium hydroxide and then with water. After air drying the crude product (62.8 g) was crystallized from 95% ethanol (800 mL) to give 34.3 g (61%) of slightly yellow crystals, mp 105-6° [Lit. 105°, Davis 00].

4-Hydroxy-4-(6-methoxynaphth-2-yl)-1-methylpiperidine (21)----- To a dry-ice cooled paste of **20** (30 g, 0.127 mol) in 200 mL of THF was added dropwise n-butyllithium (2.5 M in hexane, 50.6 mL, 0.127 mol, Aldrich 23,070-7) with magnetic stirring under nitrogen. During the addition the temperature of the mixture was kept below -40°. After the reaction mixture was stirred at -60 to -40° for one hour, 1-methyl-4-piperidone (15.75 g, 0.139 mol, Aldrich 13,003-6) redistilled one month earlier, was added at such a rate that the temperature was maintained below -40°. Stirring was continued for half an hour at that temperature and 10 mL of acetic acid in 10 mL of methanol was added as the reaction mixture warmed to -10°. After 5 minutes' stirring, the solvents were removed under reduced pressure. The residue was washed with 10% sodium hydroxide and water, was dried, and was recrystallized from 1.2 L of acetonitrile to give 19.37 g (56%) of a light yellow solid **21**, mp 178.5-80°. A second crop weighed 2.15 g, mp 172-174°.

Anal. Calcd for C₁₇H₂₁NO₂: C, 75.24; H, 7.80; N, 5.16.

Found: C, 75.54; H, 7.97; N, 5.24.

4-(6-Methoxynaphth-2-yl)pyridine (5)----- A mixture of **21** (19.3 g, 71.1 mmol) and 10% Pd/C in diphenylmethane (150 mL) was heated at 235-245° for 20 hrs with stirring provided by a continuous

purge of dry nitrogen gas introduced through an glass tube reaching almost to the bottom of the flask. During the first few hours violent bubbling occasionally occurred as water droplets from the dehydration reaction fell back into the hot solvent from the walls of the short path distillation head through which the exit gasses passed. The reaction mixture was cooled, filtered through celite in a sintered-glass funnel. The Pd/C was washed thoroughly with methylene chloride. The filtrate was distilled under reduced pressure to remove the methylene chloride and the diphenylmethane (bp 82-105°/0.5 torr). Upon cooling, the residue crystallized during two yours, and the liquid was removed with a pipette. This solid which remained was recrystallized twice from 1,2-dimethoxyethane to give 5.1 g of light yellow solid, mp 153.5-156°. This was recrystallized once again to give the analytical sample, 3.5 g, mp 155-156.5°. All the mother liquors were combined and gave a second crop of 3.3 g (mp 144-149°) brought the yield of **5** to 41%.

{YXQ-1-29}

Uv (MeOH, 1×10^{-5} M): 221 nm (44,000), 262 (41,000), 309 (19,000).

Anal. Calcd for $C_{16}H_{13}NO$: C, 81.68; H, 5.57; N, 5.95.

Found: C, 81.60; H, 5.43; N, 5.83.

4-(6-Methoxynaphth-2-yl)-1-(3-sulfopropyl)pyridinium zwitterion (5A)-----To a hot solution of **5** (1.5 g 6.38 mmol) in benzonitrile (5 mL) was added 1,3-propane sultone (1.2 g, 9.6 mmol, Aldrich P5,070-6). The solution was heated to 180° for 10 mins. and was allowed to cool slowly to room temp. The solid product which separated was collected by filtration, was washed with methyl-t-butyl ether, and was recrystallized from 200 mL of absolute ethanol to give 1.90 g (83 %) of **5A** as a yellow solid, mp 295-297° (dec). {YXQ-1-34}

Uv: 5×10^{-5} M): 225 nm (40,000), 260 (15,000), 289 (15,000), 370 (20,000).

Anal. Calcd for $C_{19}H_{19}NO_4S$: C, 63.85; H, 5.36; N, 3.92.

Found: C, 64.44; H, 5.61; N, 3.89.

4-(6-Methoxynaphth-2-yl)-1-methylpyridinium methane-sulfonate (5B)-----To a solution of **5** (1.5 g, 6.38 mmol) in acetonitrile (17 mL) was added methyl methanesulfonate (2.1 g, 19.1 mmol, Aldrich 12,992-5). The mixture was refluxed for 46 hrs as the disappearance of the starting material was monitored by tlc (1,2-dimethoxyethane /silica gel; only the starting material moves.) The

addition of toluene to the hot solution caused the separation of a gum which was induced to crystallize. The solid was collected by filtration and washed with toluene to give 1.2 g, mp 184-6°. One recrystallization from acetonitrile (10 mL) gave 0.63 g of yellow solid, **5B**, mp 194-5°. {YXQ-1-30}

Uv (MeOH, 5×10^{-5} M): 225 nm (42,000), 259 (16,000), 286 (17,000), 367 (20,000).

Anal. Calcd for $C_{18}H_{19}NO_4S$: C, 62.59; H, 5.54; N, 4.06.

Found: C, 62.01; H, 5.75; N, 3.92.

4-(4-Chlorophenyl)pyridine (22)-----Into a one-liter three-necked flask fitted with a condenser, a thermometer, and a magnetic stirrer was placed freshly ground magnesium turnings (16.5 g, 0.522 moles, 30% excess). The flask was flamed for 10 min. at 110° under nitrogen before the temperature was allowed to decrease to 40°. THF (30 mL) was added, and the mixture was brought to reflux. To the boiling solution was added dropwise a solution of 4-bromochlorobenzene (100 g, 0.522 moles, Lancaster 2745) in THF (150 mL) at such a rate as to maintain the solution at reflux. After all the aryl halide had been added, the reaction was heated to reflux for an additional two hours.

The temperature was slowly decreased to 30° and 4-chloropyridine hydrochloride (28.0 g, 0.186 moles, Aldrich C7,022-3) mixed with $PdCl_2 \cdot dppb$ (1.0044 g, 0.0018 mol) were added in small quantities, while the temperature was maintained below 50°. Stirring was continued for another 18 hrs. An additional 100 ml of THF was added in portions to the mixture during this period. The reaction was quenched by the dropwise addition of methanol (1eq, 17 ml). All solvents were stripped off under reduced pressure in a rotary evaporator. Hydrochloric acid (2M) was added to the oily residue until the pH was 2. The mixture was extracted with methylene chloride (3 x 30 ml) to remove some dichlorobiphenyl. The aqueous layer was treated with small portions of saturated sodium bicarbonate until the pH was 8. The mixture was then extracted with portions of methylene chloride (4 x 30 mL) and the combined organic layer was dried with anhydrous sodium carbonate. The solution was filtered and the solvent stripped off under reduced pressure to leave 31.0 g of crude oily product. The oil was distilled under vacuum at a temperature of 90-110°(0.1 mm Hg) using

an oil bath. After a forerun of chlorobenzene (2 g) and the main distillate weighed 24 g. This was dissolved in 10% HCl upon heating, was filtered hot, and was cooled to room temp. The hydrochloride salt was basified with a saturated solution of sodium bicarbonate. The crystals, which formed after crushed ice was added to the basic solution, were filtered and washed with water. The dried product (21.2 g) was recrystallized from hot n-hexane (70 mL) to give after filtration 18 g of crystalline **22**, mp 70-71° (51% yield) [lit. mp 70-71°, Butterworth 40].

4-[4-(6-Methoxynaphth-2-yl)phenyl]pyridine (6)-----A 250 mL flask charged with 1.02 g (42 mmol) of magnesium was heated to 200° for 15 min using a thermowell. After the flask was cooled to room temperature, 10 g (42 mmol) of 2-bromo-6-methoxynaphthalene and 100 mL of dry THF were added. Almost all of the magnesium dissolved while the mixture was refluxed with stirring for six hours. The solution was cooled to room temp and 4 g (21 mmol) of 4-(4-chlorophenyl)pyridine, 350 mg of nickel acetylacetonate (Aldrich 28,365-7) and 30 mL of THF were added. The mixture was refluxed with stirring for 17 hrs, was quenched with methanol, and was evaporated to dryness under reduced pressure. The residue was triturated with methanol and filtered to give 9 g of solid. The solid was extracted with methylene chloride (400 mL) in a Soxhlet extractor for 3 days. Evaporation of the extract gave 7.25 g of solid. Extraction of the solid with cyclohexane in a Ace-Kau column containing neutral alumina gave 4.2 g (32 %) of product mp 251-255°

Anal. Calcd for C₂₂H₁₇NO: C, 84.86; H, 5.50; N, 4.50

Found: C, 85.00; H, 5.45; N, 4.35

4-[4-(6-Methoxynaphth-2-yl)phenyl]-1-sulfopropylpyridinium zwitterion (6A)----- A mixture of 1.0 g (3.21 mmol) of 4-[4-(6-Methoxynaphth-2-yl)phenyl]pyridine **6** and 25 mL of benzonitrile was heated with mechanical stirring. After the solid dissolved 1,3-propane sultone (1.0 g, 8.1 mmol) was added. A yellow precipitate immediately separated from the hot solution, and the mixture was stirred for 1 hour at ca. 80°. After standing at room temperature overnight, the mixture was filtered. The solid was washed with acetonitrile and diisopropyl ether to give 1.4 g of **6A** as a yellow solid, mp. 366-70° (dec.)

A 1.17 g portion of **6A** was recrystallized from 400 mL of DMF with a hot filtration to give on cooling 0.86g of yellow solid, mp 268-70° which was resubmitted for elemental analysis. {YXQ-1-68}

Anal. Calcd for C₂₅H₂₃NO₄S: C, 69.26; H, 5.35; N, 3.23.

Found: C, 69.40, H, 5.37; N, 3.47.

2-(4-Methoxyphenyl)-9,9-dipropylfluorene (23)----- To a solution of 10 g (34.8 mmol) of bromide **14** and 180 mg of PdCl₂(dppb) was added 95 mL (114 mmol) of anisylmagnesium bromide in THF (1.2 M, Alfa 89435). The mixture was heated to reflux under nitrogen with stirring. After cooling to about 50° another 10 g (34.8 mmol) of **14** was added and the mixture was refluxed for 2 hrs. Then 20 mL of methanol was added to decompose the excess Grignard reagent. The mixture was evaporated to dryness. Then MeOH was added, and the solid was filtered and washed with MeOH. The 27.8 g of crude product was extracted with cyclohexane in and Ace-Kau column packed with 15 g of silica gel and 80 g of alumina to give 16 g of white crystals, mp 116-7.5° [In an earlier preparation of **23**, an analytical sample melting at 118-8.5° did not give acceptable results (Ghiorghis, 88)].

{YXQ-1-32}

Uv (cyclohexane) 265nm (31,000); 291 (31,000)

Anal. Calcd for C₂₆H₂₈O: C, 87.59; H, 7.92.

Found: C, 87.64, H, 7.79.

2-Bromo-7-(4-methoxyphenyl)-9,9-dipropylfluorene (24)-----To a solution of 15 g of **23** in 150 mL of propylene carbonate and 85 mL of CH₂Cl₂ was added 7.8 g of NBS. The cloudy solution cleared in half an hour, and stirring was continued overnight. A negative starch-iodine test showed the absence of positive halogen. Water (400 mL) and 300 mL of CH₂Cl₂ were added. The lower layer was washed with water (3x 500), 5% NaOH (500 mL) and water (3x 500 mL). The solvent was removed under reduced pressure. The residue was triturated with 3 mL of 95% EtOH, and 16.8 g of white solid, mp 114-20° was collected. The solid was recrystallized from 430 mL of 95% EtOH to give 12.9 g of solid, mp 120-127°. Recrystallization from n-hexane gave **24** as a white solid, mp 128-30° {YXQ-1-40}

Anal. Calcd for C₂₆H₂₇BrO: C, 71.72; H, 6.25.

Found: C, 71.87; H, 6.30.

4-Hydroxy-4-(7-[4-methoxyphenyl]-9,9-dipropylfluoren-2-yl)-1-methylpiperidine (25)-----To a solution of bromide **24** (6.5 g, 14.9 mmol) in 40 mL of THF was added dropwise 6 mL (15 mmol) of n-butyllithium with stirring under nitrogen below -40°. The thick mixture was stirred for 30 mins with continued cooling and 1.9 g of 1-methyl-4-piperidone was added at such a rate that the temperature did not exceed -30°. The temperature was warmed gradually to -10° before 6 mL of MeOH was added. The mixture was evaporated to remove the solvents. The residue was triturated with 100 mL of 5% NaOH, washed with water and dried (IR lamp). The 6.46 g of crude solid was recrystallized from 180 mL of toluene to give 2.38 g of very light yellow solid, mp 233-35°. The mother liquor on concentration to 40% of its volume gave on cooling 1.5 g of a second crop, mp 230-232°. The combined product was recrystallized from 150 mL of toluene to give 3.5 g of solid, mp 237-9°. A second recrystallization from 120 mL of toluene gave 3.45 g of **25**, mp 239.5-241°. {YXQ-1-42}

Anal. Calcd for C₃₂H₃₉NO₂: C, 81.83; H, 8.37; N, 2.98.

Found: C, 81.58; H, 8.16; N, 2.82.

4-(7-[4-Methoxyphenyl]-9,9-dipropylfluoren-2-yl)pyridine (7)-----A mixture of **25** (3.0 g, 6.59 mmol), 0.5 g of 10% Pd/C, and 40 mL of diphenylmethane was heated at 220-240° for 18 hrs while a stream of nitrogen gas was bubbled through the solution to sweep out the reaction byproducts. The reaction mixture was cooled and filtered through celite/sintered glass, and the catalyst was washed with several portions of CH₂Cl₂. The filtrate was evaporated to remove CH₂Cl₂ and was distilled under reduced pressure (bp 85° at 0.05 torr) to remove most of the diphenylmethane. The residue was triturated with cold acetonitrile and the solid was filtered and washed with acetonitrile. After drying the solid weighed 2.5 g, mp 179-205°. The solid was extracted from a Soxhlet cup with hot ethanol for 64 hrs. The extract was boiled down to 30 mL and the crystals obtained on cooling weighed 1.44 g, mp 177-80°. Recrystallization from acetonitrile gave 1.04 g, of **7** as a yellow solid, mp 180-182°.

{YXQ-1-47}

Anal. Calcd for C₃₁H₃₁NO: C, 85.87; H, 7.21; N, 3.23.

Found: C, 86.11; H, 7.21; N, 3.18.

4-(7-[4-Methoxyphenyl]-9,9-dipropylfluoren-2-yl)-1-sulfopropylpyridinium zwitterion (7A)-----To a hot solution of 0.6 g (1.38 mmol) of **7** in 5 mL of benzonitrile was added 0.5 g (4.0 mmol) of 1,3-propane sultone. The mixture was stirred at 180° for 30 mins. and allowed to cool slowly. The precipitate was filtered and washed with acetonitrile to give 400 mg of **7A**, mp 314-6°. The filtrate was diluted with 25 mL of methyl t-butyl ether and an additional 400 mg of yellow precipitate was obtained. The combined solids on recrystallization from 20 mL of absolute ethanol gave 0.63 g of **7A**, mp 320.5-1° (dec). {YXQ-1-48}

Anal. Calcd for C₃₄H₃₇NO₄S: C, 73.48; H, 6.71; N, 2.52.
Found: C, 73.22, H, 6.77; N, 2.39.

LIST OF PUBLICATIONS AND TECHNICAL REPORTS

No publications have as yet resulted from this work. A semi-annual progress report (3 pp) covering the Period of March 1, 1990 to June, 30, 1990 was submitted to ARO in August 1990.

LIST OF PARTICIPATING SCIENTIFIC PERSONNEL

During the period of March 1990 through February 1991 only two persons worked on the syntheses reported here: Charles J. Kelley (P.I.) and Yuanxi Qin (postdoctoral associate). No students received degrees for this or related work during the extended period of the contract. However, two graduate students, Rajini Pothapu and Ravindra Ganesan, worked on the synthesis of compound **14** during a course with the P.I. in Organic Synthesis.

INVENTIONS

No inventions have arisen from the work reported here.

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